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INFLUENCE OF THE ISOTHERMAL ANNEALING ON THE FREE VOLUME CHANGES IN THERMO-SHRUNKEN POLYETHYLENE BY POSITRON ANNIHILATION

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Positron lifetime measurements in polyethylene have been performed. Samples of the polyethylene were isothermally annealed at three temperatures (373 K, 423 K, and 473 K) for different time periods (from 5 min to 5 h). After cooling, the samples were used for the lifetime measurements in air at room temperature. A conventional fast-slow coincidence lifetime spectrometer with plastic scintillators has been used to perform the lifetime measurements. Mean free volumes radii and fractional free volume have been calculated from the lifetime data.

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1. Introduction

Positron annihilation spectroscopy is widely used for investigations of different aspects of polymer properties [1, 2] and positron behaviour in polymers. The thermalised positron can annihilate with an electron from the absorber or it may form, with this electron, a bound system — positronium (Ps). In amorphous regions of a polymer substance free volumes exist, where *ortho*-positronium (*o*-Ps) may live for several ns. Many different external conditions can perturb the fate of the positron in polymer matter and due to this, they might change its lifetime. Polyethylene (PE) is one of the most common polymers. It is used all over the world for different purposes. It is also investigated by numerous authors [3–8]. The purpose of this paper was to investigate the influence of the isothermal annealing on the free volume changes in thermo-shrunk PE.

2. Experimental

2.1. The spectrometer and the source characteristics

A conventional slow-fast coincidence spectrometer with plastic scintillators has been used. The time resolution of the spectrometer, approximated by two

Gaussian curves, has been determined by analysing the measurements of the positron lifetimes in Kapton foils. Typical values of the full widths at half of the maximum (FWHM_i) have been as follows: FWHM_1 about 257 ps and I_1 about 70%; FWHM_2 about 360 ps. Positron lifetime spectra have been accumulated to approximately $(2.5) \times 10^6$ counts. A positron source (about 0.2 MBq) was sealed between two Kapton foils (8 μm thick). The source correction has been taken into account during numerical evaluations. All of the measurements have been performed in air at room temperature. The measurements have been repeated at least twice for each sample. The values of the parameters obtained after numerical analyses of the raw lifetime spectra have been reproducible.

2.2. The samples

All of the measured samples were made of PE produced by the Institute of Nuclear Chemistry and Technology, Warsaw (Poland) as thermo-shrunk sheets used for electric cables insulation. This Institute used granules of Lupolen 2012D, schwarz 413 (made by BASF) for production of the sheets. The density of the granules was 0.933–0.939 g/cm³. The samples (9 mm in diameter) were cut down from a 1.3 mm thick sheet. The positron source was sandwiched between two pairs of such discs. Three different types of samples were used for investigations. The samples of first type were cut down from the sheet of the PE without any modification during the technological process (they are described in the paper: the as-produced samples). The samples of the second type were prepared from the sheet of the PE irradiated by electrons during the production process, they are described in the article: the irradiated samples. Finally, the third types were made of the “orientated” PE sheet (it means the sheet was lengthened in the course of production process at elevated temperature). These types of the samples are described in the article: the orientated samples. The samples were isothermally annealed, at three different temperatures (373 K, 423 K, and 473 K) before the measurements, in an oven, in air. Annealing at higher temperatures caused melting of the samples. The time of the annealing was also changed (from 0 min, the non-annealed sample to 300 min). Additional measurements for thermal characterisation of the samples were performed by differential scanning calorimetry (DSC), a heating rate: 20 K/min. The melting (T_m) points were defined as the maximum of the melting endotherm (of the DSC trace). For all the investigated samples $T_m = (381 \pm 5)$ K.

3. Results

The positron lifetime spectra were analysed using the package programs PATFIT-88 [9]. These programs have fitted four exponential components to the measured spectra. No constraints on lifetimes and intensities have been imposed during numerical calculations. The longest-lived component, τ_4 , is attributed to the pick-off annihilation of *o*-Ps. According to the model proposed by Tao [10] and Eldrup et al. [11], the longest-lived component of the positron lifetime spectrum may be correlated with the mean radius of the free volume cavity in the polymer matter. They derived the following equation:

$$\tau_4 = 0.5 \{1 - R/(R + 0.1656) + (1/2\pi) \sin[2\pi R/(R + 0.1656)]\}^{-1}, \quad (1)$$

where τ_4 is the *o*-Ps lifetime expressed in nanoseconds, R is the mean radius of the spherical well expressed in nm, and 0.1656 nm is an empirical constant.

The aim of this investigation was to find out a relation between the annealing parameters of the thermo-shrunk PE and the mean radius of the free volume cavity. This is the reason why only τ_4 , I_4 , and R values (calculated according to Eq. (1)) are listed, as the results of this investigation, in Tables I, II, and III, for three types of the samples, respectively.

TABLE I

τ_4 , I_4 , and R values obtained for the as-produced samples.

Anne- aling time [min]	τ_4 [ps]	I_4 [%]	R [nm]	τ_4 [ps]	I_4 [%]	R [nm]	τ_4 [ps]	I_4 [%]	R [nm]
	Annealing temperature								
	373 K			423 K			473 K		
0	2587 ± 20	21.88 ± 0.47	0.333 ± 0.002	2587 ± 20	21.88 ± 0.47	0.333 ± 0.002	2587 ± 20	21.88 ± 0.47	0.333 ± 0.002
5	2616 ± 22	21.14 ± 0.51	0.336 ± 0.002	2620 ± 21	21.72 ± 0.51	0.336 ± 0.002	2615 ± 20	21.71 ± 0.50	0.336 ± 0.002
10	2580 ± 23	22.07 ± 0.61	0.333 ± 0.002	2643 ± 23	21.45 ± 0.57	0.338 ± 0.002	2617 ± 18	21.72 ± 0.42	0.336 ± 0.001
15	2575 ± 22	22.20 ± 0.56	0.333 ± 0.002	2618 ± 21	22.01 ± 0.53	0.336 ± 0.002	2600 ± 29	20.76 ± 0.74	0.334 ± 0.002
30	2632 ± 19	21.46 ± 0.45	0.337 ± 0.001	2616 ± 18	21.84 ± 0.41	0.336 ± 0.001	2559 ± 17	21.97 ± 0.40	0.331 ± 0.001
60	2647 ± 20	21.56 ± 0.47	0.338 ± 0.001	2575 ± 24	21.78 ± 0.65	0.333 ± 0.002	2577 ± 24	21.85 ± 0.61	0.333 ± 0.002
120	2606 ± 18	21.94 ± 0.38	0.335 ± 0.001	2569 ± 18	22.23 ± 0.43	0.332 ± 0.001	2599 ± 19	22.12 ± 0.46	0.334 ± 0.001
180	2612 ± 20	21.95 ± 0.48	0.335 ± 0.002	2624 ± 20	20.97 ± 0.47	0.336 ± 0.002	2595 ± 19	22.61 ± 0.50	0.334 ± 0.002
240	2595 ± 17	22.18 ± 0.41	0.334 ± 0.001	2593 ± 21	20.75 ± 0.48	0.334 ± 0.002	2631 ± 29	21.32 ± 0.80	0.337 ± 0.002
300	2654 ± 29	20.62 ± 0.72	0.338 ± 0.002	2590 ± 23	21.41 ± 0.58	0.334 ± 0.002	2596 ± 21	21.85 ± 0.52	0.334 ± 0.002

TABLE II

 τ_4 , I_4 , and R values obtained for the irradiated samples.

Anne- aling time [min]	τ_4 [ps]	I_4 [%]	R [nm]	τ_4 [ps]	I_4 [%]	R [nm]	τ_4 [ps]	I_4 [%]	R [nm]
	Annealing temperature								
	373 K			423 K			473 K		
0	2540 ± 20	19.89 ± 0.42	0.330 ± 0.002	2540 ± 20	19.89 ± 0.42	0.330 ± 0.002	2540 ± 20	19.89 ± 0.42	0.330 ± 0.002
5	2543 ± 20	21.21 ± 0.48	0.330 ± 0.002	2564 ± 28	21.79 ± 0.77	0.332 ± 0.002	2590 ± 22	22.31 ± 0.57	0.334 ± 0.002
10	2566 ± 20	21.59 ± 0.47	0.332 ± 0.002	2551 ± 18	22.79 ± 0.43	0.331 ± 0.001	268 2 ± 24	21.51 ± 0.60	0.341 ± 0.002
15	2565 ± 17	20.97 ± 0.37	0.332 ± 0.001	2579 ± 30	21.84 ± 0.89	0.333 ± 0.002	2677 ± 25	21.50 ± 0.62	0.340 ± 0.002
30	2552 ± 18	22.17 ± 0.42	0.331 ± 0.001	2588 ± 27	21.98 ± 0.77	0.334 ± 0.002	2638 ± 24	22.74 ± 0.66	0.337 ± 0.002
60	2584 ± 19	21.23 ± 0.45	0.333 ± 0.001	2574 ± 23	22.37 ± 0.61	0.333 ± 0.002	2668 ± 22	22.15 ± 0.55	0.340 ± 0.002
120	2577 ± 19	22.11 ± 0.48	0.333 ± 0.001	2612 ± 33	21.83 ± 0.98	0.335 ± 0.003	26 67 ± 20	22.59 ± 0.49	0.339 ± 0.002
180	2573 ± 22	21.56 ± 0.57	0.33 2 ± 0.002	2572 ± 25	22.11 ± 0.69	0.332 ± 0.002	2603 ± 60	22.99 ± 1.96	0.335 ± 0.004
240	2587 ± 19	21.79 ± 0.45	0.333 ± 0.001	2605 ± 23	22.14 ± 0.59	0.335 ± 0.002	2528 ± 18	22.53 ± 0.65	0.329 ± 0.001
300	2535 ± 16	22.40 ± 0.37	0.329 ± 0.001	2573 ± 20	22.39 ± 0.49	0.332 ± 0.002	2573 ± 18	20.12 ± 0.37	0.332 ± 0.001

TABLE III

 τ_4 , I_4 , and R values obtained for the orientated samples.

Annealing time [min]	τ_4 [ps]	I_4 [%]	R [nm]	τ_4 [ps]	I_4 [%]	R [nm]	τ_4 [ps]	I_4 [%]	R [nm]
	Annealing temperature								
	373 K			423 K			473 K		
0	2609 ± 20	21.62 ± 0.46	0.335 ± 0.001	2609 ± 20	21.62 ± 0.46	0.335 ± 0.001	2609 ± 20	21.62 ± 0.46	0.335 ± 0.001
5	2628 ± 18	22.11 ± 0.42	0.337 ± 0.001	2648 ± 20	21.82 ± 0.48	0.338 ± 0.002	2648 ± 15	21.16 ± 0.32	0.338 ± 0.001
10	2656 ± 22	21.89 ± 0.55	0.339 ± 0.002	2609 ± 19	22.26 ± 0.46	0.335 ± 0.001	2603 ± 19	21.37 ± 0.45	0.335 ± 0.002
15	2623 ± 18	22.46 ± 0.43	0.336 ± 0.001	2625 ± 22	21.94 ± 0.54	0.336 ± 0.001	2625 ± 17	21.48 ± 0.37	0.336 ± 0.001
30	2636 ± 19	22.19 ± 0.47	0.337 ± 0.001	2619 ± 22	21.70 ± 0.55	0.336 ± 0.002	2610 ± 17	21.41 ± 0.37	0.335 ± 0.001
60	2607 ± 15	22.50 ± 0.35	0.335 ± 0.001	2616 ± 20	21.85 ± 0.47	0.336 ± 0.001	2598 ± 21	21.50 ± 0.49	0.334 ± 0.002
120	2615 ± 18	22.13 ± 0.44	0.336 ± 0.001	2631 ± 27	21.84 ± 0.70	0.337 ± 0.002	2571 ± 19	22.06 ± 0.48	0.332 ± 0.002
180	2601 ± 17	22.22 ± 0.39	0.335 ± 0.001	2660 ± 46	20.66 ± 1.30	0.339 ± 0.003	2622 ± 17	22.17 ± 0.37	0.336 ± 0.001
240	2633 ± 18	22.45 ± 0.43	0.337 ± 0.001	2629 ± 20	21.46 ± 0.47	0.337 ± 0.001	2545 ± 19	20.39 ± 0.41	0.330 ± 0.002
300	2626 ± 20	22.00 ± 0.48	0.336 ± 0.002	2611 ± 25	21.40 ± 0.63	0.335 ± 0.002	2541 ± 21	18.72 ± 0.42	0.330 ± 0.002

Typical values of the shorter lifetimes and their intensities, for the as-produced samples, were as follows: $\tau_1 = (180 \pm 25)$ ps, $I_1 = (20 \pm 10)\%$, $\tau_2 = (375 \pm 25)$ ps, $I_2 = (45 \pm 15)\%$, $\tau_3 = (1050 \pm 150)$ ps, $I_3 = (7.5 \pm 1.5)\%$. Within these error bars are included all fitted values of the measurements parameters obtained for ten different annealing times and for three different annealing temperatures. The parameters of the annealing process (its temperature and time) were quite different but the R and I_4 values do not change remarkably, except for the samples annealed at 473 K.

Equation (1) has allowed us to combine the mean radius of the spherical well with the concept of the specific or fractional free volume in polymers. This fractional free volume, denoted by f , is defined as

$$f = (V - V_0)/V = V_f/V, \quad (2)$$

where V is the total macroscopic volume of the polymer, V_0 is the volume occupied by molecules, V_f is the free volume of the polymer. The fractional free volume might

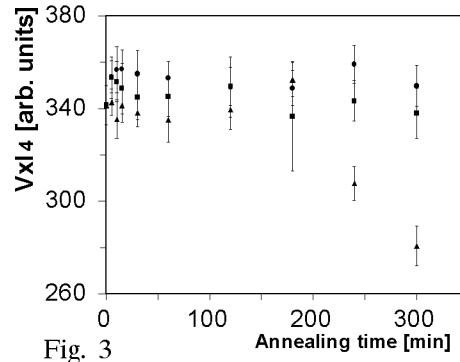
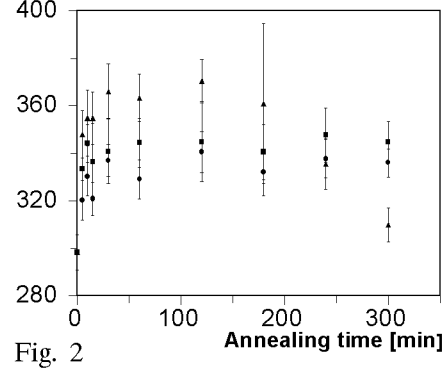
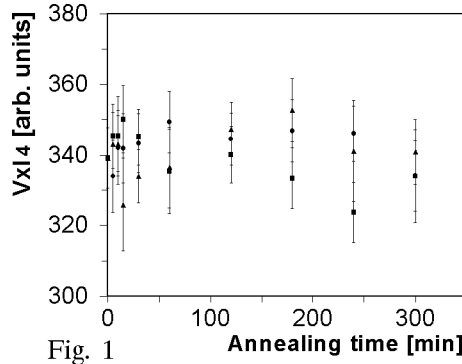


Fig. 1. The $(V \times I_4)$ values for the as-produced samples vs. the annealing time at different temperatures (\bullet — 373 K, \blacksquare — 423 K and \blacktriangle — 473 K).

Fig. 2. The $(V \times I_4)$ values for the irradiated samples vs. the annealing time at different temperatures (\bullet — 373 K, \blacksquare — 423 K and \blacktriangle — 473 K).

Fig. 3. The $(V \times I_4)$ values for the orientated samples vs. the annealing time at different temperatures (\bullet — 373 K, \blacksquare — 423 K and \blacktriangle — 473 K).

be determined from the lifetime measurements. The relative intensity of the *o*-Ps lifetime component, I_4 , is assumed to be proportional to the number of the free volume holes because it gives the information on the *o*-Ps formation probability. Wang et al. [12] and Kobayashi et al. [13] proposed a semiempirical relation which may be used to evaluate the fractional free volume f

$$f = A \times I_4 \times V_{\text{sph}}, \quad (3)$$

where I_4 is the relative intensity of the *o*-Ps lifetime component, $V_{\text{sph}} = (4\pi R^3/3)$ [nm³] is free volume of the single hole (the R value is taken from Eq. (1)), A is the normalisation constant. The A value has not been measured in this work but as it is the constant, the f value must be proportional to the product: $(I_4 \times V_{\text{sph}})$. In Figs. 1, 2, and 3 the evaluations of this product are shown for three types of the measured samples. It is clear that for the as-produced samples there is no correlation between the f values and both the annealing time and the annealing temperatures. Experimental points are randomly distributed about $f = 337 \pm 15$. Similarly, for the irradiated samples there is no tendency between the f values and the time and the temperature annealing at 373 K and 423 K. However f drops with the time annealing for the samples annealed at 473 K from about $f = 355 \pm 10$ to about $f = 310$. This decrease starts after 180 min of the time annealing. The same behaviour was observed for the orientated samples. The f values for the samples annealed at 373 K and 427 K level off at about $f = 350 \pm 15$. On the contrary, the experimental points for the samples annealed at 473 K show a tendency with the time. The f drops from about 335 to about 280 for the annealing time longer than 180 min. Kobayashi et al. [13] and Madani et al. [14] observed a similar effect of the decreasing f in poly(vinyl acetate) and in epoxy, respectively. As τ_4 is proportional to the overlap of the positron and electron wave function in a free volume cavity it is obvious that τ_4 will be correlated with the dimension of that cavity. The behaviour of the f values for the as-produced samples suggests that the material of the samples was resistant to the changes of the temperatures and time annealing. Even for the highest (used in the investigation) temperatures and the longest time annealing, both values R and I_4 were constant which resulted in levelling off the f values. It indicates that neither the radii of the free volume nor the *o*-Ps formation probability were influenced by thermal treating. A similar effect was observed for the irradiated and orientated samples at 373 K and 423 K. In spite of this, the decrease in the f values was observed for these samples at the temperature annealing of 473 K for the time annealing longer than 180 min (Figs. 2 and 3). As R values were almost constant for these samples it is the decrease in the relative intensity of the *o*-Ps lifetime component, I_4 , that is responsible for the decrease in f . The decrease in the f values might be explained taking into account the production process of the PE sheets. During this process polymer chains were strongly stretched, especially in the case of the orientated samples. Free volume spaces were created where *o*-Ps might live. When the samples were heated at 473 K, for longer than 3 h, the polymer chains shrank and some of the free volume disappeared. It might cause the decrease in I_4 and consequently the similar decrease in f . Unfortunately, the time annealing was no longer than 5 h, in the work. It seems that the longer thermal treatment of the samples may explain this behaviour.

4. Conclusions

Three different kinds of the thermo-shrunk PE were investigated by positron annihilation. Thermal treating of the as-produced samples does not seem to disturb the chains structure of the PE because the f values are constant. The irradiated and orientated samples show the decrease in the f values for high (473 K) temperature and long (longer than 3 h) time annealing. It is supposed that this decrease is caused by the decrease in the relative intensity of the o -Ps lifetime component, I_4 .

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